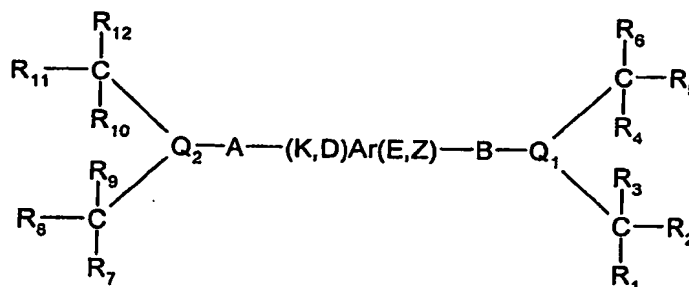


CLAIMS

1. A process for the carbonylation of C₃-C₂₀ ethylenically unsaturated compounds which process comprises reacting
 5 said C₃-C₂₀ ethylenically unsaturated compound with carbon monoxide in the presence of a source of hydroxyl groups and of a catalyst system, the catalyst system obtainable by combining:

- 10 (c) a metal of Group VIII or a compound thereof: and
 (d) a bidentate phosphine of general formula (I)



wherein:

Ar is a bridging group comprising an optionally
 15 substituted aryl moiety to which the phosphorus atoms are linked on available adjacent carbon atoms;

A and B each independently represent lower alkylene;

- 20 K, D, E and Z are substituents of the aryl moiety (Ar) and each independently represent hydrogen, lower alkyl, aryl, Het, halo, cyano, nitro, OR¹⁹, OC(O)R²⁰, C(O)R²¹, C(O)OR²², NR²³R²⁴, C(O)NR²⁵R²⁶, C(S)R²⁵R²⁶, SR²⁷, C(O)SR²⁷, or -J-Q³(CR¹³(R¹⁴)(R¹⁵))CR¹⁶(R¹⁷)(R¹⁸) where J represents lower
 25 alkylene; or two adjacent groups selected from K, Z, D and E together with the carbon atoms of the aryl ring to which they are attached form a further phenyl ring, which is

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optionally substituted by one or more substituents selected from hydrogen, lower alkyl, halo, cyano, nitro, OR¹⁹, OC(O)R²⁰, C(O)R²¹, C(O)OR²², NR²³R²⁴, C(O)NR²⁵R²⁶, C(S)R²⁵R²⁶, SR²⁷ or C(O)SR²⁷;

R¹ to R¹⁸ each independently represent lower alkyl, aryl, or Het;

R¹⁹ to R²⁷ each independently represent hydrogen, lower alkyl, aryl or Het;

Q¹, Q² and Q³ (when present) each independently represent phosphorous, arsenic or antimony and in the latter two cases references to phosphine or phosphorous above are amended accordingly ;

wherein the carbonylation reaction is carried out at a temperature of between -30°C to 49°C and under a CO partial pressure of less than 30 x 10⁵ N.m⁻².

2. A process according to claim 1, wherein R¹ to R¹⁸ each independently represent C₁ to C₆ alkyl, C₁-C₆ alkyl phenyl (wherein the phenyl group is optionally substituted as defined herein) or phenyl (wherein the phenyl group is optionally substituted as defined herein).

3. A process according to claims 1 or 2, wherein R¹ to R¹⁸ each independently represent non-substituted C₁ to C₆ alkyl such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl and cyclohexyl.

4. A process according to any preceding claim, wherein each of the groups R¹ to R³, R⁴ to R⁶, R⁷ to R⁹, R¹⁰ to

R¹², R¹³ to R¹⁵ or R¹⁶ to R¹⁸ together independently may form cyclic structures such as adamantyl, 1-norbornyl or 1-norbornadienyl.

5. A process according to any preceding claim, wherein
5 each R¹ to R¹⁸ group represents the same lower alkyl, aryl, or Het moiety as defined herein.
6. A process according to any preceding claim, wherein, each R¹ to R¹⁸ represents methyl.
7. A process according to any preceding claim, wherein
10 each Q¹, Q² and Q³ (when present) represents phosphorous.
8. A process according to any preceding claim, wherein
15 in the compound of formula I, A, B and J (when present) each independently represent C₁ to C₆ alkylene which is optionally substituted as defined herein.
9. A process according to any preceding claim, wherein the lower alkylene which A, B and J may independently represent is -CH₂- or -C₂H₄-.
10. A process according to any preceding claim, wherein
20 K, D, E or Z independently represents hydrogen.
11. A process according to any preceding claim, wherein
25 two of K, D, E and Z together with the carbon atoms of the aryl ring to which they are attached form a phenyl ring, the phenyl ring being optionally substituted with one or more substituents selected from aryl, lower alkyl (which alkyl group may itself be optionally substituted or terminated as defined
30 below), Het, halo, cyano, nitro, OR¹⁹, OC(O)R²⁰, C(O)R²¹, C(O)OR²², NR²³R²⁴, C(O)NR²⁵R²⁶, SR²⁷, C(O)SR²⁷ or C(S)NR²⁵R²⁶ wherein R¹⁹ to R²⁷ each independently represent hydrogen or lower alkyl (which alkyl group

may itself be optionally substituted or terminated as defined herein).

12. A process according to any preceding claim, wherein the hydroxyl group containing compound includes water or an organic molecule having a hydroxyl functional group.
13. A process according to claim 12, wherein, the organic molecule having a hydroxyl functional group may be branched or linear, and comprises an alkanol, particularly a C_1 - C_{30} alkanol, including aryl alkanols, which may be optionally substituted with one or more substituents selected from lower alkyl, aryl, Het, halo, cyano, nitro, OR^{19} , $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)R^{25}R^{26}$, SR^{27} or $C(O)SR^{27}$ as defined herein. Highly preferred alkanols are C_1 - C_8 alkanols such as methanol, ethanol, propanol, iso-propanol, iso-butanol, t-butyl alcohol, n-butanol, phenol and chlorocapryl alcohol.
14. A process according to any preceding claim, wherein the carbonylation of an ethylenically unsaturated compound as defined herein may be performed in one or more aprotic solvents.
15. A process according to any of claims 1-12, wherein the reaction is carried out in the absence of any external aprotic solvent ie. an aprotic solvent not generated by the reaction itself.
16. A process according to any preceding claim, wherein the process is carried out with the catalyst comprising a support.
17. A process according to any claim 15, wherein the support material is porous silica which has a surface area in the range of from 10 to 700 m^2/g , a total pore volume in the range of from 0.1 to 4.0 cc/g and

an average particle size in the range of from 10 to 500 μm .

18. A process according to any preceding claim, wherein the organic groups R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} and R^{12} when associated with their respective carbon atom form composite groups which are at least as sterically hindering as t-butyl.
19. A process according to claim 1, wherein the bidentate ligands are selected from bis (di-t-butyl phosphino)-o-xylene (also known as 1,2 bis (di-t-butylphosphinomethyl) benzene); 1,2 bis (diadamantylphosphinomethyl) benzene; 1,2 bis (diadamantylphosphinomethyl) naphthalene; 1,2 bis (di-t-pentyl phosphino)-o-xylene (also known as 1,2 bis (di-t-pentyl-phosphinomethyl) benzene); and bis 1,2 (di-t-butyl phosphino) naphthalene.
20. A process according to any preceding claims 1-18, wherein suitable Group VIIIB metals or a compound thereof which may be combined with a compound of formula I include cobalt, nickel, palladium, rhodium and platinum.
21. A process according to claim 19, wherein suitable compounds of such Group VIII metals include: salts of such metals with, or compounds comprising weakly coordinated anions derived from, nitric acid; sulphuric acid; lower alkanolic (up to C_{12}) acids such as acetic acid and propionic acid; sulphonic acids such as methane sulphonic acid, chlorosulphonic acid, fluorosulphonic acid, trifluoromethane sulphonic acid, benzene sulphonic acid, naphthalene sulphonic acid, toluene sulphonic acid, e.g. p-toluene sulphonic acid, t-butyl sulphonic acid, and 2-hydroxypropane sulphonic acid; sulphonated ion

exchange resins; perhalic acid such as perchloric acid; halogenated carboxylic acids such as trichloroacetic acid and trifluoroacetic acid; orthophosphoric acid; phosphonic acids such as benzenephosphonic acid; and acids derived from interactions between Lewis acids and Broensted acids; the optionally halogenated tetraphenyl borate derivatives; zerovalent palladium complexes particularly those with labile ligands; or tri(dibenzylideneacetone)dipalladium.

22. A process according to claim 20, wherein the anion may be derived from or introduced as one or more of an acid having a pKa measured in aqueous solution at 18°C of less than 4.
23. A process according to any preceding claims, wherein the carbonylation is carried out at a temperature of between -10 to 45°C.
24. A process according to any preceding claim, wherein the carbonylation is carried out at a CO partial pressure of less than $15 \times 10^5 \text{ N.m}^{-2}$.
25. A process according to any preceding claim, wherein the reaction is carried out on ethylenically unsaturated C₃-C₂₀ compounds.
26. A process according to any preceding claim, wherein the ethylenically unsaturated compound is an alkene having 1, 2, 3 or more carbon-carbon double bonds per molecule.
27. A process according to any preceding claim, wherein the ethylenically unsaturated compound may, when there are sufficient number of carbon atoms, be linear or branched, be substituted, be cyclic, acyclic or part cyclic/acyclic, and/or be optionally substituted or terminated by one or more substituents

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selected from lower alkyl, aryl, alkylaryl, Het, alkylHet, halo, OR¹⁹, OC(O)R²⁰, C(O)R²¹, C(O)OR²², NR²³R²⁴, C(O)NR²⁵R²⁶, NO₂, CN, SR²⁷ wherein R¹⁹ to R²⁷ each independently represent hydrogen or lower alkyl.

- 5 28. A process according to any preceding claim, wherein the ethylenically unsaturated compounds may be independently selected from ethene, propene, 1-butene, 2-butene, isobutene, 1-pentene, 2-pentene, 3-pentene and branched isomers thereof, 1-hexene and
10 its isomers, 1-heptene and its isomers, 1-octene and its isomers, 1-nonene and its isomers, 1-decene and its isomers, the C₁₁-C₂₀ alkenes and their known isomers, 3-pentenitrile, methyl-3-penteneoate, 1,3 butadiene, 1,3-pentadiene, 1,3 hexadiene, 1,3
15 cyclohexadiene, 2,4-leptadiene, 2-methyl 1,3 butadiene.
29. A process for the carbonylation of ethylenically unsaturated compounds as hereinbefore described and with reference to the examples.
- 20 30. An acid or ester produced by the carbonylation of an ethylenically unsaturated compound in accordance with the present invention.
31. An acid or ester as hereinbefore described and with reference to the examples.

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